

Revised

DEPARTMENT OF CHEMISTRY

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Notre Dame, Indiana

NASA CR 55169

First Status Report on Grant NsG339

National Aeronautics and Space Administration

by

Professor G. F. D'Alelio

I. Preliminary Experiments

Prior to receipt of the grant, preliminary experiments performed between the period of April 17, 1962 and June 8, 1962, confirmed that the reaction of the following specific dicarbonyl compounds, terephthaldehyde, glyoxal and benzophenone reacted in solution with the following specific polyamino compounds, diaminobenzene and benzoguanamine to produce conjugated polymeric Schiff's bases. The polymers obtained ranged in color from yellow to orange to dark brown and all of them were infusible. This synthesis from solution yields the polymers in the form of "brick dust polymers" which were not fabricable; they could not be dissolved or melted.

Other preliminary experiments confirmed also that these specific dicarbonyl and polyamino compounds could be reacted in a melt thereby passing through a fusible, soluble stage, which could be interrupted only at early degrees of polymerization. Using the melt process, black conjugated polymers were obtained which were of higher molecular weight than those obtained by the solution process.

II. Research Under the Grant

The deficiencies of the solution and melt process indicated that since the polymerization reaction between the amine and the aldehyde was too rapid and too difficult to control, a new approach to the preparation of the polymer was

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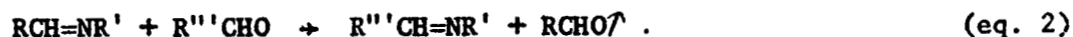
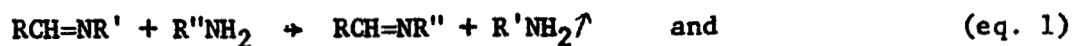
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required. The new approach was to decrease the reactivity of (a) the amine, or (b) the carbonyl compound or (c) both. This new approach has resulted in the discovery of a new chemical reaction which we have termed the Schiff's Base Exchange. This reaction is not described in the literature either as an ordinary organic reaction or as a polymerization reaction. Before applying this new reaction to polymerization reactions, it was established and confirmed as a definite chemical reaction applicable to the syntheses of ordinary Schiff's Bases.

A. The New Schiff's Base Exchange Reaction

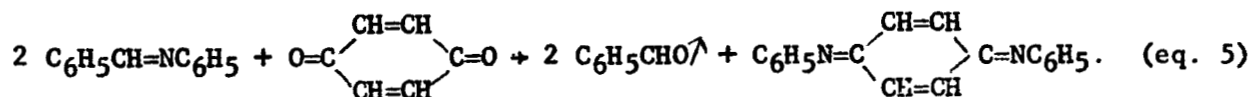
This reaction may be expressed generally by equations 1 and 2:



This Schiff's Base Exchange Reaction was proven in non-polymer systems, by a reasonable number of reactions and was dramatically illustrated by the following examples:

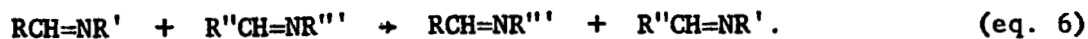


This reaction was then extended in an extraordinary way to the quinones, thus



B. The bis-Schiff's Base Exchange

The discovery of this base exchange reaction led to the consideration of the possibility of a bis-Schiff's Base Exchange which would involve reacting two Schiff's bases and exchanging the groups within the bases, thus



Confirmation of this bis-reaction was left to be tested in the preparation of the polymers.

C. Polymerizations Using the New Schiff's Base Exchange Reaction

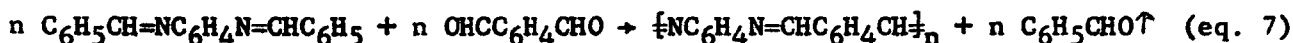
The average functionality, \bar{f} , of the reagents used in equations 1 to 6

inclusive is much less than 2, and therefore incapable of producing polymers. The applicability of this new reaction to produce polymers was first checked by using the reagents $\text{C}_6\text{H}_5\text{CH}=\text{NC}_6\text{H}_4\text{N}=\text{C}_6\text{H}_5$ and $\text{OCHC}_6\text{H}_4\text{CHO}$, both of which have a potential δ of 2.

The applicability of the new reaction for the preparation of conjugated polymers was confirmed on the first experiment, in which the polymerization passes through a controllable viscous, soluble, fusible state which can be interrupted to isolate a fusible polymer which can be further polymerized in the molten and solid state to high molecular weights.

1. Polymerization Using an Aldehyde Exchange

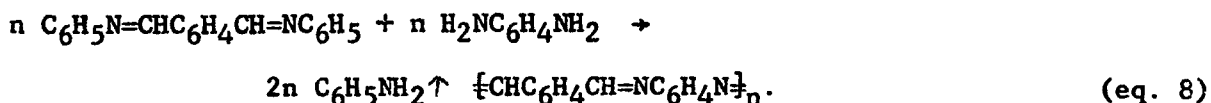
This polymerization reaction is represented by equation 7 wherein an aldehyde is exchanged in the reaction, thus:



The final polymer obtained is jet black, tough and does not melt at red heat.

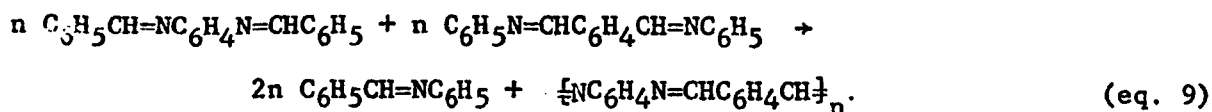
2. Polymerization Using an Amine Exchange

The applicability of this exchange reaction was further verified with a system inverse to that of equation 7 by using a system wherein the amine is exchanged, as represented by equation 8.



3. Polymerization Using a Bis Exchange

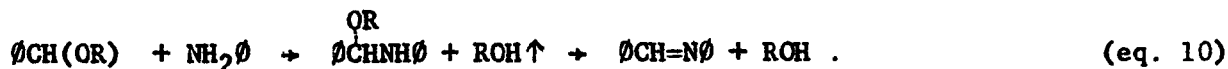
Novel as the reactions represented by equations 7 and 8 may be, more startling still was the polymerization reaction accomplished through a bis-Schiff's base exchange wherein two interrelated Schiff's bases were exchange-condensed to produce (1) a conjugated Schiff's base polymer and (2) a by-product Schiff's base as illustrated by equation 9



These important discoveries and their possible patentability were discussed with Mr. Bernard Achhammer, NASA Headquarters, Washington, and who suggested that the immediate program be concentrated on exploring the depth and breadth of this new polymerization reaction to allow NASA to protect these results with patent applications, if NASA so desired. Mr. Achhammer also requested a preliminary tabulation of the possible patent applications resulting from the work to date be made part of this report for which see Item III.

D. New Acetal Syntheses for Conjugated Polymeric Schiff's Bases

As an alternate to the Schiff's Base Exchange, it was conceived that the reactivity of the aromatic aldehyde to aromatic amines might be reduced if they were first converted to the acetal, which then could be used to prepare a Schiff's base. The postulated non-polymeric reaction is illustrated by equation 10



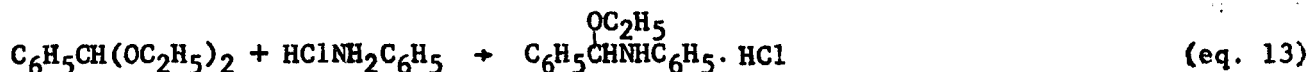
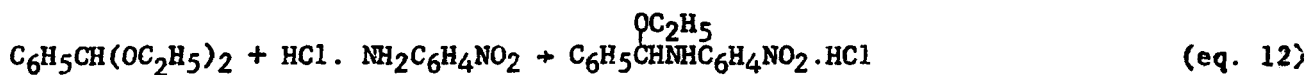
This reaction for aromatic compounds has not been described in the literature.

It was also hoped that the intermediate product of the reaction, $\text{OCHNH}\overset{\text{OR}}{\text{O}}$, could be isolated.

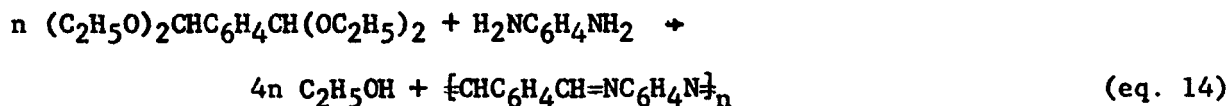
At this time we can report that we have confirmed the synthesis of non-polymeric Schiff's bases by use of the acetals instead of the aldehydes. This was proven by the synthesis of benzyl anilide as given in equation 11.



We were not able, however, in a reasonable number of uncatalyzed reactions, to isolate or identify the postulated intermediate, $\text{C}_6\text{H}_5\overset{\text{OC}_6\text{H}_5}{\text{CHNHC}_6\text{H}_5}$ since the reaction proceeds to the final product as given in equation 11. However, by use of the amine hydrochloride, it now appears that it is possible to isolate or identify the intermediate as the hydrochloride as indicated with p-nitroaniline and aniline according to equations 12 and 13 respectively:



At present, the synthesis of the tetraacetal of terephthalaldehyde, $(\text{C}_2\text{H}_5\text{O})_2\text{CHC}_6\text{H}_4\text{CH}(\text{OC}_2\text{H}_5)_2$, is underway to check the applicability of the acetal route to the synthesis of polymers as illustrated by equation 14,



E. Non-Polymerizable Schiff's Bases, $\text{ArN}=\text{CHAR}$, as Polymerization Solvents

Preliminary tests have indicated that the non-polymerizable Schiff's bases of the structure $\text{ArN}=\text{CHAR}$ wherein Ar is an aryl group are satisfactory media for the polymerization reaction leading to conjugated Schiff's bases which under other conditions precipitate as "brick dust" out of solvent systems as soon as formed. The base, $\text{C}_6\text{H}_5\text{N}=\text{CHC}_6\text{H}_5$, has been used as a solvent media for equations 7, 8 and 9.

III. The Various Patentable Aspects

A. Possible Patent Applications Assignable to NASA

1. Single Base Exchange

Case No. 1. A general application on the Schiff's Base Exchange Reaction as applicable to non-polymeric and polymeric reactions.

Case No. 2. Preparation of conjugated polymers using the amine-type Schiff's Base Exchange, e.g., $\text{ON}=\text{CH}\text{OCH}=\text{N}\text{O} + \text{H}_2\text{N}\text{ONH}_2 \rightarrow \text{polymer}$.

Case No. 3. Preparation of conjugated polymers using the aldehyde-type Schiff's Base Exchange, e.g., $\text{ON}=\text{CH}\text{OCH}=\text{N}\text{O} + \text{OHC}\text{OCHO} \rightarrow \text{polymer}$.

Case No. 4. Preparation of conjugated polymers using Schiff's Base Exchange on hydrazones, e.g.,



Case No. 5. Preparation of conjugated polymers using Schiff's Base

Exchange on glyoxal derivatives, e.g.,



Case No. 6. Preparation of conjugated polymers using Schiff's Base

Exchange of a quinoanilide, e.g.,



Case No. 7. Preparation of conjugated polymers using the Schiff's Base

Exchange based on triazines having at least two amino groups and $\text{O}=\text{N}-\text{CH}=\text{CH}-\text{N}=\text{O}$.

2. Bis-Schiff's Base Exchange

Case No. 8. A general case on preparing conjugated polymers using bis-Schiff's Base Exchange procedures, examples to be based on specific sub classes given in Cases Nos. 9, 10 and 11.

Case No. 9. Preparation of conjugated polymers using a bis-Schiff's Base Exchange for the two classes of bases



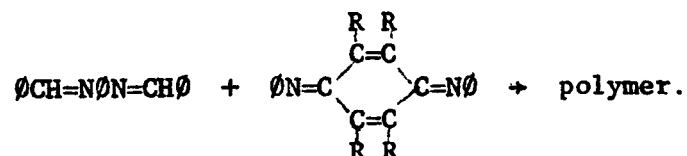
Case No. 10. Preparation of conjugated polymers using a bis-Schiff's

Base Exchange for the two classes of bases,



Case No. 11. Preparation of conjugated polymers using a bis-Schiff's

Base Exchange for the two classes



3. Non-Polymeric Schiff's Bases as Reaction Media

Case No. 12. Preparation of conjugated polymeric Schiff's Bases using non-polymeric Schiff's bases, $\text{O}=\text{CH}-\text{N}=\text{O}$ as the reaction medium.

B. Other Patentable Aspects

1. It may be possible to claim the conjugated polymeric Schiff's Bases of this research as Compositions of Matter per se. Prior to the researches of the principal investigator of this project, there were no publications which could be cited against this work. The first related but minor publication appeared as an article by J.W. Akitt, F.W. Kaye, B.E. Lee and A.M. North, *Makromolekulare Chemie*, p. 195-199, October 1962. The article was received by *Macromolekulare Chemie* for publication on July 10, 1962. Our reduction to practice dates back to the period April 17, 1962 to June 8, 1962. We are in a position, therefore, to "swear back" of this reference in the prosecution of a patent application on compositions of matter. Though this reduction to practice was prior to the date of the grant, an assignment to NASA can be considered.
2. Another possible patent application can be based on the melt process of a dicarbonyl compound and a diaryl amine which was also reduced to practice between the period of April 17, 1962 and June 8, 1962. The Akitt et al. publication discloses preparation of some conjugated Schiff's bases in solution only, and therefore is inapplicable as a reference in the prosecution of a method patent. As in the composition of matter case (III.B.1), this work was performed also prior to the grant but an assignment to NASA can be considered.

The research performed between April 17, 1962 and June 8, 1962 was performed primarily to check the correctness of the new concepts, the confirmation of which would allow presentation to a sponsor with more assurance of possible success than if presented solely as a "blue sky" proposal.

IV. Intermediates Prepared and in Preparation

The project to date has required the synthesis of a large number of chemical intermediates, and the following compounds have already been prepared in very high purity:

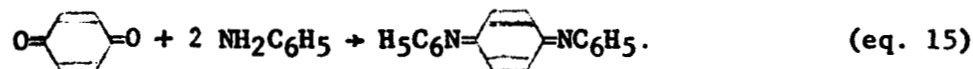
<u>Compound No. 1</u>	$\text{C}_6\text{H}_5\text{CH}=\text{NHC}_6\text{H}_5$
<u>Compound No. 2</u>	$p\text{-C}_6\text{H}_5\text{N}=\text{CHC}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_5$
<u>Compound No. 3</u>	$p\text{-C}_6\text{H}_5\text{CH}=\text{NC}_6\text{H}_4\text{N}=\text{HCC}_6\text{H}_5$
<u>Compound No. 4</u>	$m\text{-C}_6\text{H}_5\text{CH}=\text{NC}_6\text{H}_4\text{N}=\text{HCC}_6\text{H}_5$
<u>Compound No. 5</u>	$\text{C}_6\text{H}_5\text{CH}=\text{N}-\text{N}=\text{C}_6\text{H}_5$
<u>Compound No. 6</u>	$\text{C}_6\text{H}_5\text{CH}=\text{NC}_6\text{H}_4\text{C}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_5$
<u>Compound No. 7</u>	$\text{C}_6\text{H}_5\text{CH}=\text{NC}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4\text{N}=\text{CHC}_6\text{H}_5$
<u>Compound No. 8</u>	$o\text{-HOC}_6\text{H}_4\text{N}=\text{CH}-\text{CH}=\text{NC}_6\text{H}_4\text{OH}.$

At the start of the project, these compounds were prepared by the usual technique of reacting the amine and carbonyl compound in a solvent such as ethyl alcohol and accepting an equilibrium yield of 50-70%. We have now recently improved the synthesis by using a continuous toluene or xylene azeotropic method in a Starke-Dean apparatus until the theoretical amount of water is obtained to give a quantitative crude yield of the desired Schiff's base.

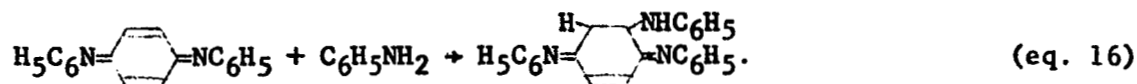
A number of other intermediate compounds have also been prepared by the solvent technique but not in the high purity desired. Such a typical compound is Compound No. 9.

Compound No. 9, $\text{C}_6\text{H}_5\text{N}=\text{C}_6\text{H}_4=\text{NC}_6\text{H}_5$

Quinone and aniline were reacted in alcohol according to equation 15



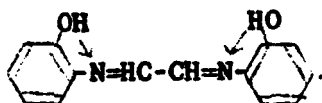
This compound is contaminated by the side reaction involving the addition of aniline to the ring, as in equation 16



Though the purity of the compound obtained under these conditions was sufficient to check its ability to undergo base exchange polymerization with phenylene diamine, its purity is not high enough for research purposes. An alternate synthesis which appears to be most promising is now under study and is based on the oxidation of commercially available p-triphenylene imine by commercial quinone according to equation 17.



Attention is directed to compound No. 8 in the above list. The parent substance for this series is $\text{H}_5\text{C}_6\text{N}=\text{CHCH}=\text{NC}_6\text{H}_5$, but all attempts to prepare it directly from glyoxal and aniline have produced aniline-type resins instead of the desired Schiff's base. By using the ortho aminophenol we were able to obtain a derivative of the parent compounds as a model compound for polymerization studies. The fact that the aminophenol did not produce resins under these conditions is attributed to stabilization due to chelation of the hydrogen of the phenolic hydroxyl with the nitrogen atoms, thus



The parent compound is still desired and studies are underway to achieve its synthesis.

To establish the breadth of the new Schiff's base exchange reaction, and the diversity and breadth of this class of polymers and of the polymerization system to assure good patent cover for NASA, a number of other compounds and intermediates (Nos. 10 to 13, inc.) are under preparation in addition to compounds 6 and 7, which have already been prepared for these reasons.

Compound No. 10, $(\text{CH}_3)_2\text{C}=\text{NC}_6\text{H}_4\text{N}=\text{C}(\text{CH}_3)_2$

To prove that a terminal aryl group is not essential in the Schiff's base intermediates of the class, $\text{ArCH}=\text{NArN}=\text{CHAR}$, but that any $=\text{C}\begin{smallmatrix} \text{R} \\ \text{R} \end{smallmatrix}$ structure is effective, there is now under preparation the diketyl derivative of p-phenylene diamine by reaction with acetone using our new azeotrope techniques as shown

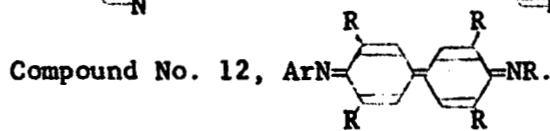
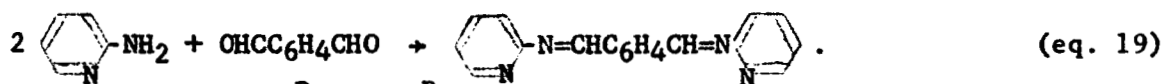
in equation 18



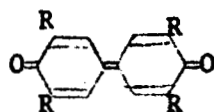
When prepared it will be reacted with suitable dicarbonyl compounds to determine if polymers are obtainable from it.

Compound 11, $\text{NC}_5\text{H}_4\text{N}=\text{CHC}_6\text{H}_4\text{CH}=\text{NC}_5\text{H}_4\text{N}$

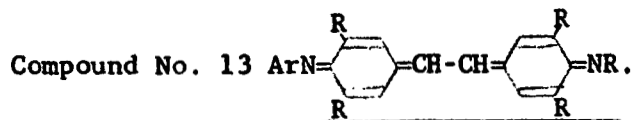
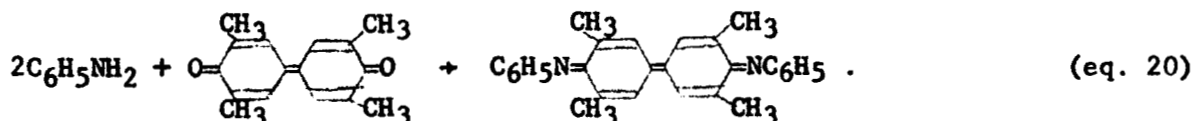
Also to prove that an anilido group is not required in the Schiff's base of the formula, $\text{C}_6\text{H}_5\text{N}=\text{CHC}_6\text{H}_4\text{CH}=\text{NC}_6\text{H}_5$, there is now under preparation the corresponding pyridine derivative by reacting terephthalaldehyde with 2-aminopyridine azeotropically according to equation 19



To extend the quinone reaction further, and to prove its applicability more widely, other types of quinones, such as naphthaquinone, etc., are being converted to Schiff's bases. Of greater interest and possibly of more importance in this problem are quinones which have conjugated aromatic rings such as

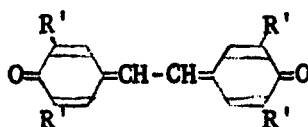


The tetramethyl derivative has been prepared and is being converted to an intermediate suitable for base exchange by our azeotropic reaction with aniline according to equation 20.

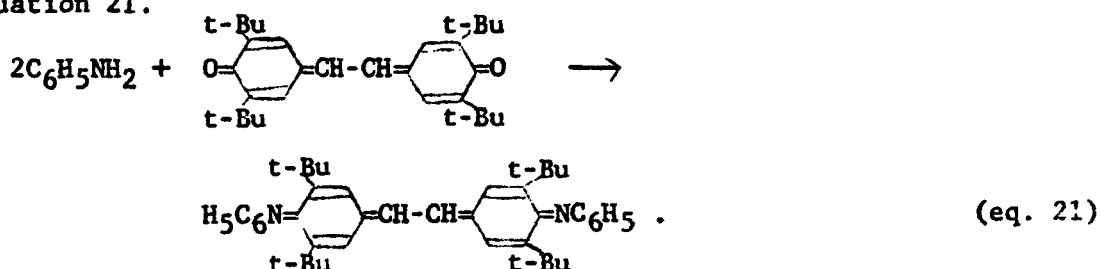


This compound is related remotely to Compound No. 12 above. It must be prepared because a determination should be made as to whether or not the quinone-type rings can be separated by non-aromatic bridges and still form suitable

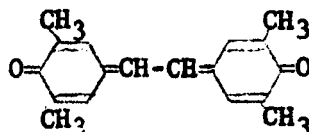
polymers. In this class of compounds, the requirement must also be met that the conjugation must not be interrupted. The class of compounds represented by Compound No. 13 appears to meet this requirement. We now have available



wherein R is a tertiary butyl group, and its reaction with aniline azeotropically will be tried. Due to the bulk factor presented by the t-butyl group, a slow rate of reaction or even a lack of reaction may be found for that expected and given by equation 21.



If the prediction of poor reactivity turns out to be true, and if the reaction given by equation 20 proceeds, we will then try to synthesize the tetramethyl derivative,



convert it to the dianilide and evaluate it in a polymerization reaction.

The tetra-t-butyl derivative is being examined first because the compound is on hand from another research problem and because the correlation of equations 21 and 20 will give us information on how bulk factors can influence not only anilide formation but also the polymerization reaction.

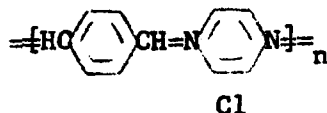
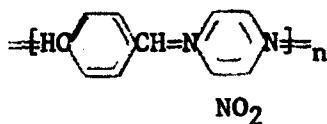
V. The Present Research Staff on the Project

G.F. D'Alelio - Director
T. Huebner - Research Associate
L. Beaulieu - Secretary
Toshikazu Kurosaki - Postdoctoral
James Crivello - Predoctoral
William Fessler - Predoctoral.

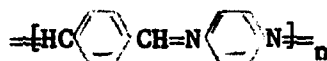
VI. Research Planned for August 1963 to February, 1964

During the next period we will (1) continue the syntheses of new monomers required to determine the breadth and limitations of (a) the Schiff's Base Exchange Reaction and (b) the types of conjugated polymeric Schiff's bases which must be made, if they can be made, to protect NASA possible patent position; (2) synthesize pure monomers and intermediates required for research on the project; (3) begin the detailed polymerization studies involving (a) the contrast of the various methods of producing the conjugated polymers, (b) the kinetics and mechanism of the reaction, (c) the establishment of appropriate methods for determining the molecular weight of the polymers obtained, etc.; (4) continue to explore the acetal process for producing the polymers; (5) undertake initial studies to determine the limit of the degree of polymerization with one or more of the conjugated polymers at which the polymer is still soluble, and/or fusible, and at which stage it can still be fabricated; (6) start to explore the semiconductor properties of the polymers. The conjugated polymers of this project are not only highly heat-resistant but also organic semiconductors, a property which we anticipated and which now has been confirmed. (See the Macromolecular Chemistry reference under Item III-B).

Our concepts include the introduction of electron-withdrawing and electron-donating groups on the segments of the polymer. Accordingly, we will attempt the synthesis of a few such substituted polymers to compare their semiconductor properties with the unsubstituted parent polymers. Most probably, we will attempt the synthesis of one or both of the following polymers:



for comparison with the parent polymer,



VII. Future Program

The preliminary investigations carried out under this grant have opened up new and promising areas of research and development in the field of heat-resistant polymers and organic semiconductors. There is little or no background in the technical literature in the areas under study, and this requires that we have to develop our own fundamental knowledge on (1) the Schiff's base exchange, (2) the acetal synthesis, (3) the structure and syntheses of new monomers, (4) the effect of structure and substitution on the electrical and semiconductor properties of the derived polymers, (5) the methods of determining molecular weights, etc.